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Response Surface Methodology for optimizing Process Parameters for Synthesis of Carbon Nanotubes

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Abstract

Response surface methodology was employed to optimize the synthesis parameters for Carbon nanotubes. Such optimization was undertaken to ensure a high efficiency over the experimental ranges employed and to evaluate the interactive effects of the temperature, catalyst amount, and volume of carbon for synthesis of Multi-walled carbon Nanotubes (MWCNTs) from methylated ester of *Helianthus annuus* oil on silica supported Fe/Mo catalyst by spray pyrolysis method. A total of 17 experimental runs were carried out employing the detailed conditions designed by response surface methodology based on the Box- Behnken design. The experimental confirmation tests showed a correlation between the predicted and experimental responses. The optimal point obtained was located in the valid region and the optimum adsorption parameters were predicted as a temperature of 668 ^{0} C, a precursor volume of 21ml and catalyst weight of 0.78 g. Under these conditions, a highest yield of 75% was achieved from spray pyrolysis method.

Key words: Spray pyrolysis; Carbon nanotubes; Box-Behnken design.

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1. INTRODUCTION

In the emerging field of nanomaterials, carbon nanotubes have potential significance (Iijima, 1991). Carbon nanotubes have outstanding electrical, thermal and mechanical properties, which make them interesting material for applications in nanoelectronics, sensors, field emission and as reinforcing agents in composite materials (Mamalis et al. 2004). The most important methods developed to produce carbon nanotubes include electric arc discharge, laser ablation and chemical vapour deposition (Ebbesen et al. 1992; Endo et al. 1995; Thess et al. 1996). The CVD method has attracted attention due to possibility to produce nanotubes on a commercial scale. To date, only purified petroleum products such as methane, benzene, acetylene etc. are in practice for synthesizing CNTs (Cui et al. 1999; Fan et al. 1999; Kong et al. 1998; Li et al. 1996; Sen et al. 1997; Wei et al. 2002). Several Botanical hydrocarbons such as camphor, turpentine oil & eucalyptus oil were found to be good carbon source for synthesis of CNTs (Kumar et al. 2003; Pradip Ghosh et al. 2007; Afre et al. 2005). We have succeeded in growing of carbon nanotubes from methylated ester of *Helianthus annuus* oil a botanical hydrocarbon. *Helianthus annuus* oil was found to be a promising precursor for CNT synthesis.

Response surface methodology (RSM) can avoid the limitations of conventional methods and is commonly used in many fields. The main purpose of RSM is to check the optimum operational conditions for a given system or to determine a region that satisfies the operational specifications (Montgomery et al. 2000). Meyyappan's group has achieved considerable success in high throughput combinatorial screening of several catalysts and growth parameters for nanotubes production (Cassell et al. 2001; Cassell et al. 2003; Ng Ht et al. 2003). While these results are very valuable from the fundamental research point of view, the method itself is not suitable for fast entry-level optimization. In the present study we prove that the Box-Behnken experimental design can be utilized successfully for the rapid optimization of spray pyrolysis process parameters of carbon nanotubes growth. We take a Fe/Mo/silica – *Helianthus annuus* oil system as our starting point, identify the key factors affecting MWCNTs yield by a fractional factorial screening design and fit the response surface using a Box-Behnken design.

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2. EXPERIMENTAL

$Fe(NO_3)_3.9H_2O$ and $(NH_4)Mo_7O_{24}.4H_2O$ were dissolved in methanol and mixed thoroughly with methanol suspension of silica (Merck). The solvent was then evaporated and the resultant cake heated to 90-100 °C for 3 hours, removed from the furnace and ground in an agate mortar. The fine powders were then calcined for 1 hour at 450 °C and then re-ground before loading into the reactor. The catalyst was placed on the quartz boat. The boat was placed in the heating furnace. The carrier gas nitrogen (100 ml/min) was flushed out before switch on the reaction furnace to remove air and create nitrogen atmosphere.

The temperature was raised from room temperature up to the desired growing temperature. Waiting was done for 10 minutes for stabilization of temperature. Subsequently, each 20ml of methylated ester of *Helianthus annuus* oil was introduced into the quartz tube through spray nozzle and the flow was maintained using saline tube at the rate of 0.5 ml/min for each precursors. The deposition time lasted for 45 minutes for each deposition at temperature range of 550 - 750°C. The reactor was then allowed to cool to room temperature with nitrogen gas flowing. The carbon product on the silica support was then weighed to determine the carbon yield of the spray pyrolysis. We define carbon yield here as the functional mass increase $(m_1-m_0)/m_0$, where m_1 and m_0 are, respectively, the final mass of the catalyst support with carbon deposit and the initial mass of the catalyst support. Of course, not all the carbon mass is in the form of MWNTs. Nevertheless, the amount of amorphous carbon detected in electron microscope images was small and our practical definition of the relative yield is believed to provide a reasonable assessment of MWNTs production in these experiments.

The as-grown MWNTs were purified by 40 mg of raw material was added to 20 ml 1N HCl to form an acidic slurry. This slurry was heated to 60°C and stirred at 600 rpm. To this heated acidic slurry 20 ml H_2O_2 was added to form oxidative slurry that continued to be heated and stirred for 30 minutes. The addition of HCl, H_2O_2, subsequent heating and stirring was repeated three more times, each time allowing the heated oxidative slurry to stir for 30 minutes. Phase separation was allowed to proceed followed by filtering the carbon phase and washing with 1N HCl and distilled water. The collected sample was dried at 120 °C in hot air oven for 2 hours. The morphology of the sample was characterized by HRTEM, and Raman spectroscopy.

3. EXPERIMENTAL DESIGN

The process parameters affecting the synthesis of MWCNTs were studied using RSM combined with the three-level, three-factorial Box-Behnken experimental design. The variable input parameters were Temperature of 550 ^{0}C - 750 ^{0}C (A), Volume of carbon feedstock in the range of 10-30ml (B) and catalyst amount in the range of 0.5-1g(C) , the factor levels being coded as -1 (low), 0 (medium) and +1 (high) respectively. The range and levels used in the experiments are listed in Table 1.

Table 1: Independence Factors and their coded levels used for optimization

Variable	Real values of coded levels	
	Low	High
Temperature in deg Celsius	550	750
Volume of carbon feedstock in ml	10	30
Catalyst amount in g	0.5	1

Table 2: The Box-Behnken design for the three independent variables

Run	Factor 1 Temp , Deg Celsius	Factor 2 Volume of carbon feedstock , ml	Factor 3 Catalyst amount , gm	Response Yield ,%
1	0.00	0.00	0.00	30
2	-1.00	0.00	-1.00	73
3	1.00	1.00	0.00	71
4	0.00	1.00	1.00	35
5	0.00	0.00	0.00	50
6	0.00	0.00	0.00	15
7	0.00	-1.00	-1.00	50
8	0.00	0.00	0.00	30
9	0.00	1.00	-1.00	20
10	-1.00	0.00	1.00	35
11	-1.00	1.00	0.00	17
12	1.00	-1.00	0.00	74
13	1.00	0.00	1.00	10
14	-1.00	-1.00	0.00	75
15	0.00	0.00	0.00	12
16	0.00	-1.00	1.00	40
17	1.00	0.00	-1.00	73

In Table 2, a total of 17 runs were performed to optimize the process parameters and experiments were carried out according to the actual experimental design matrix. The results were analyzed applying the coefficient of determination (R^2) , analysis of variance (ANOVA) and response plots. Several methods including Transmission electron microscopy, Raman spectroscopy have been suggested for assessing the quality of carbon nanotube samples.

4. RESULTS AND DISCUSSION

The quadratic equation for predicting the optimal point was achieved according to the Box-Behnken experimental design and input variables , and the empirical relationship between the response and the independent variables in the coded units based on the experimental results was given by

$$Y = 73.20+9.75A-2.25B+0C+2.5AB-0.50AC+12BC-31.60A^2-19.10B^2-16.10C^2$$

The results from the ANOVA for the quadratic equation are presented in Table 3. The ANOVA suggests that the equation and the actual relationship between the response and the significant variables represented by the equation were adequate. The larger the value of F and the smaller the value of p, the more significant is the corresponding coefficient term (Amini et al. 2008; Kalavathy et al. 2009). The value of p was lower than 0.05, indicating that the model may be considered to be statistically significant. For the synthesis of CNTs, the ANOVA results (Table 3) indicated that the F-value for the model was 81.37, implying that most of the variation in the response could be explained by the regression equation and that the model was significant. Furthermore, the probability $p<0.0001$ also suggested that the model was significant. In this study, A, BC, $A^{2,}$ B^2 and C^2 were significant parameters.

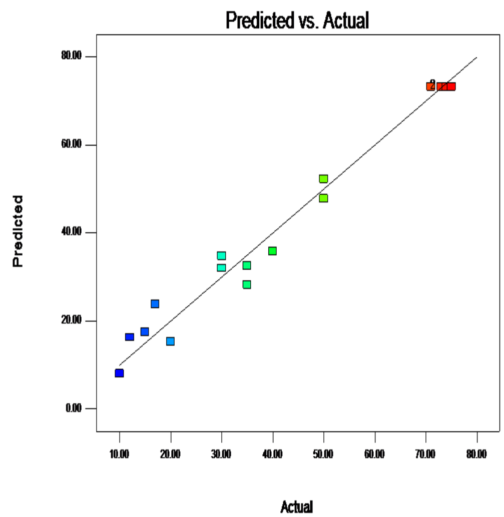

Fig. 1. : Plot of the actual and predicted values

The data were also analyzed to check the correlation between the experimental and predicted yield (Y in %) as shown in Fig.1.

Table 3: ANOVA for response surface quadratic model

Source	Sum of Squares	df	Mean Square	F Value	p-value
Model	8943.2588	9	993.6954	32.84168	< 0.0001
A-Temp	760.5	1	760.5	25.13456	0.0015
B-Volume of carbon	40.5	1	40.5	1.338526	0.2852
C-catalyst	0	1	0	0	1.0000
AB	25	1	25	0.826251	0.3936
AC	1	1	1	0.033050	0.8609
BC	576	1	576	19.03682	0.0033
A^2	4204.4631	1	4204.4631	138.9577	< 0.0001
B^2	1536.0421	1	1536.0421	50.76626	0.0002
C^2	1091.4105	1	1091.4105	36.07116	0.0005
Residual	211.8	7	30.257142		
Lack of Fit	203	3	67.66666	30.75757	0.0032
Pure Error	8.8	4	2.2		
Cor Total	9155.0588	16			

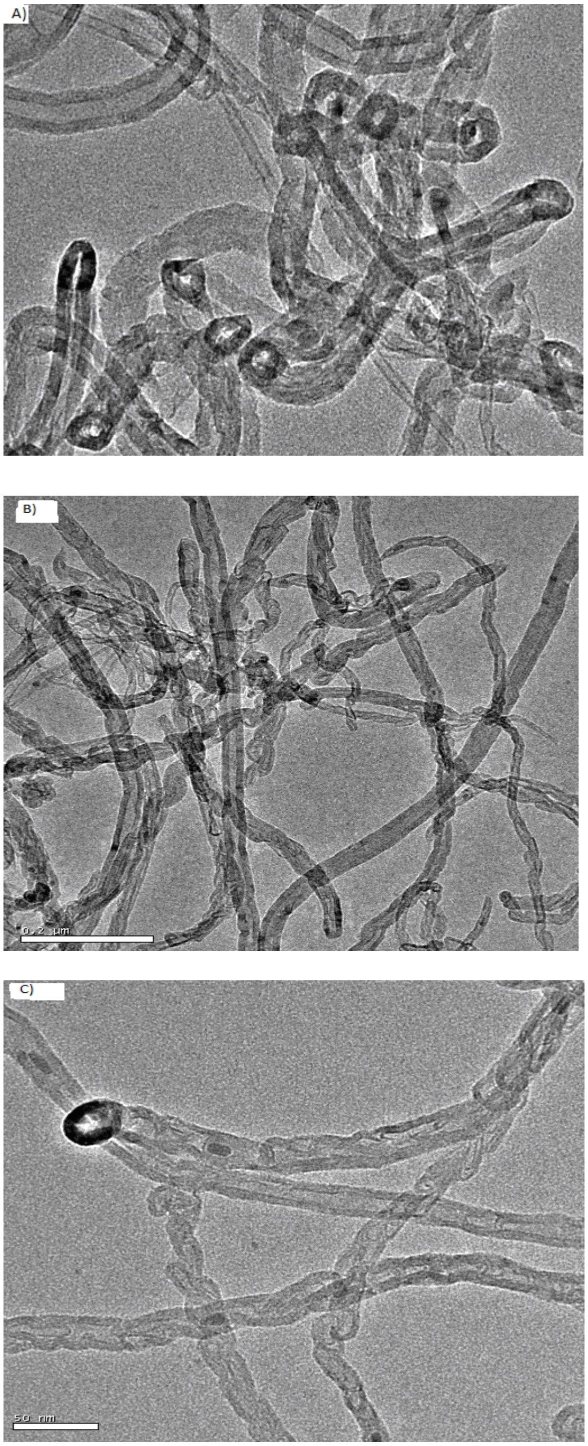

Fig 2: HRTEM image of as grown multiwalled carbon nanotubes in different Temperatures A) 550^0 B)650^0 C, C)750 ^{0}C

The experimental values were the measured response data for the runs designed by the Box-Behnken model, while the predicted values were obtained by calculation from the quadratic equation. It can be seen from Figure1 that the data points on the plot were reasonably distributed near to the straight line, indicating a good relationship between the experimental and predicted values of the response, and that the underlying assumptions of the above analysis were appropriate. The result also suggests that the selected quadratic model was adequate in predicting the response variables for the experimental data.

A characteristic HRTEM image of the sample was depicted in Fig. 2. The sample consists of Multiwalled carbon nanotubes and carbon debris. Based on our previous experience with nanotube synthesis, we included the following process variables in the optimization: i) reaction temperature, ii) volume of carbon feedstock, iii) catalyst amount .

Efficient optimization requires the early identification of key process parameters. This can be achieved by assuming that all parameters generate a predominantly linear response which is measured by setting each parameter to a low, medium and high value. In the present study, we performed seventeen runs arranged in a 2^3_{III} fractional facorial design. This arrangement allows the rapid screening of the whole parameteric spectrum which were selected. Sample synthesized in this screening series are presented in Fig. 2. Raman spectroscopy is wildly used to characterize the structural and phase disorder information in carbon related material. The well crystallization of the grapheme layer conformed from I_G/I_D ratio (Fig.3). The I_G/I_D ratio increases with increase of temperature range from 550 °C to 650 °C. But further increase of temperature to 750 °C results in degree of I_G/I_D ratio. Thus the quality Carbon nanotubes were formed the reaction temperature at 650 °C.

4.1. Three-dimensional response surface plot

The three-dimensional response surface plots, obtained as a function of two factors maintaining all other factors constant, are helpful in understanding both the main effects and the interaction effects of these two factors (Adinarayana et al. 2002).

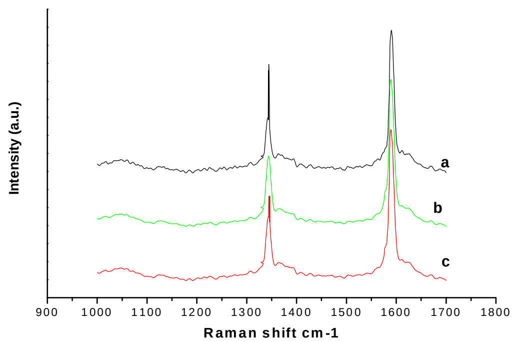

Fig. 3: Raman spectrum of as grown carbon nanotubes in different temperature a) 550 °C b) 650 °C and c) 750 °C.

The three-dimensional response surface plots and related contour plots are depicted in Fig. 4 & 5 respectively. The response surface plots in Figures are part of a parabolic cylinder, exhibiting a minimum and maximum ridge, respectively, in the investigated domain. In each response surface, the optimum values of both variable factors, such as the Temperature (A), Volume of the carbon (B) and catalyst amount (C) could be analyzed by the sadle point or by determining the maxima formed by the x and y coordinates.

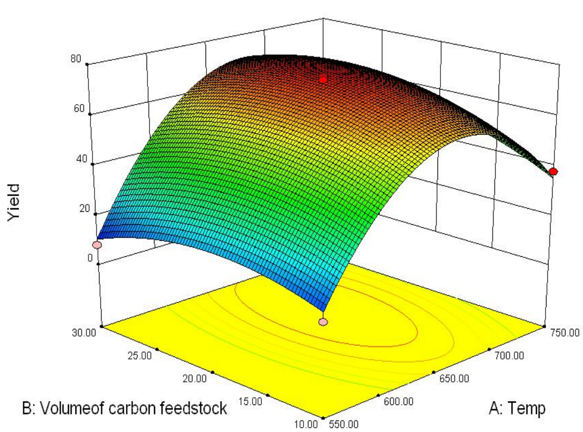

Fig. 4: Response surface plot for the effects of Volume of carbon and Temperature

Fig. 5 depicts the three-dimensional response surface relationship between volume of carbon feedstock on the production of highest yield of MWCNTs. The combined effect of temperature and catalyst amount on the CNT yield by spray pyrolysis method at constant volume of carbon feedstock is depicted in Fig. 5. From this figure, as the catalyst amount was increased from 0.5 to 0.8, an increase occurred in the yield followed by the yield decreased as the catalyst weight was increased further.

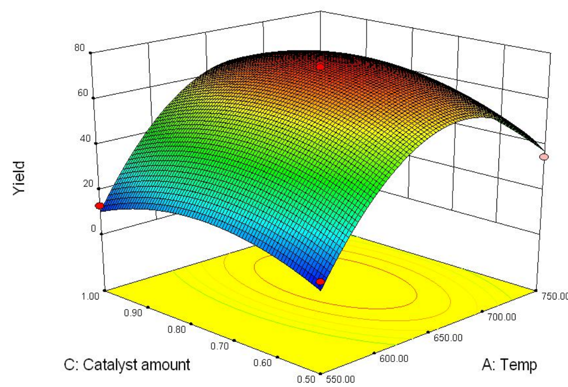

Fig 5: Response surface plot for the effects of Catalysts and Temperature

4.2. Numerical optimization

One of the primary objectives of the present study was to find the optimum process paramaters for maximizing the yield of MWCNTs. The model capable of predicting the maximum yield showed that the optimum values of the process variables were a Temperature of 668 ^{0} C, Volume of carbon feedstock of 21 ml and catalyst amount of 0.78 g. Under these conditions, the predicted yield was 74% which was in good agreement with the experimental value of 75 %.

5. CONCLUSIONS

Multiwalled carbon nanotubes were synthesized from a natural precursor Helianthus annuus oil . The response surface modelling was successfully combined with the Box-Behnken design to determine the effects of several important process parameters, such as temperature, volume of carbon feedstock and catalyst amount to enable the optimization of MWNTS yield over the experimental range examined.

Through ANOVA by the second-order polynomial regression equation, it was shown that the temperature and volume of carbon feedstock had the significant effects on yield. Process optimization was conducted and a maximum predicted yield was 74% was obtained at the temperature of 668 ^{0}C, volume of carbon feedstock of 21 ml and a catalyst amount of 0.78g. The present study has shown that RSM combined with a Box-

Behnken design provides a very reliable and accurate methodology for optimizing experiments for the yield of MWCNTs by spray pyrolysis method.

6. ACKNOWLEDGEMENTS

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